

National Performance Audit Program
Ambient Air Audits of Analytical
Proficiency, 1981

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NATIONAL PERFORMANCE AUDIT PROGRAM
AMBIENT AIR AUDITS OF ANALYTICAL PROFICIENCY
-1981-

by

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ABSTRACT

This report presents the results of the U.S. Environmental Protection Agency's 1981 National Audit Program, which are summarized by pollutant and by analytical method. Semiannual audits were conducted for SO_2 and NO_2 (bubbler methods), Pb, NO_3 and $\text{SO}_4^{=}$ (filter strips) and CO (continuous monitors). One audit was conducted on high-volume flow rate. Continuous SO_2 monitors were audited throughout the year, such that no monitor was audited more than once. Approximately 60 laboratories participated in each SO_2 bubbler audit and 50 in each NO_2 bubbler audit. Approximately 60 laboratories participated in each $\text{SO}_4^{=}$ audit, 50 in each NO_3 audit and 97 in each Pb audit. Approximately 380 CO monitors were checked in each CO audit and 159 continuous SO_2 monitors were checked throughout the year. A total of 1,462 flow devices were audited. Approximately 6 percent of the overall results were rejected as statistical outliers. This value is consistent with that observed in previous audits.

CONTENTS

	<u>Page</u>
Abstract.	iii
Tables	vi
Acknowledgments	vii
1. Introduction	1
2. Summary and Conclusions	4
3. Audit Materials	5
4. Audit Results	9
References	10

TABLES

<u>Number</u>		<u>Page</u>
1	Agency Participation	13
2	Audits Results for Sulfur Dioxide	14
3	Results for the Pararosaniline Method	15
4	Percent of Sulfur Dioxide Measurements within Indicated Percent of Assigned Value	16
5	Audit Results for Nitrogen Dioxide	17
6	Audit Results for Nitrogen Dioxide by the Sodium Arsenite Method	18
7	Percentage of Nitrogen Dioxide Measurements Within Indicated Percent of Assigned Value	19
8	Audit Results for Carbon Monoxide	20
9	Audit Results for Carbon Monoxide by the NDIR and GC Methods	21
10	Percentage of Carbon Monoxide Measurements Within Indicated Percentage of Assigned Value	22
11	Audit Results for Sulfate on Filter Strips	23
12	Audit Results for Sulfate by the Manual Methods	24
13	Audit Results for Sulfate by the Automated Method	25
14	Percentage of Sulfate Measurements Within Indicated Percentage of Assigned Value	26
15	Audit Results for Nitrate on Filter Strips	27
16	Audit Results for Nitrate by the Automated Methods	28
17	Percentage of Nitrate Measurements Within Indicated Percentage of Assigned Value	29
18	Audit Results for Lead on Filter Strips	30
19	Percentage of Lead Measurements Within Indicated Percentage of Assigned Value	31
20	Audit Results for Sulfur Dioxide Continuous Monitors	32
21	Audit Results for Sulfur Dioxide Continuous Monitors by Various Instrumental Methods	33
22	Audit Results for High-Volume Flow Rate	34

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SECTION 1

INTRODUCTION

The 1981 ambient air audits of analytical proficiency, which were managed by the Environmental Monitoring Systems Laboratory (EMSL), of the U.S. Environmental Protection Agency (EPA), are a part of a continuing audit program of six ambient air pollutants and high-volume samplers. The program, entitled the National Performance Audit Program, allows EPA to monitor the performance of laboratories making air pollution measurements and participating agencies to assess their performance with respect to other agencies. The audits are conducted by the Quality Assurance Division (QAD) of EMSL, Research Triangle Park, North Carolina. Inquiries and applications to participate should be directed to this address.

Agencies participating in the audits are solicited by the EPA Regional Quality Control Coordinator in each of EPA's 10 regions. Once a laboratory enrolls in a particular audit, it is automatically notified of subsequent audits of that pollutant. Participants are assigned a permanent identifying code number. Federal, state, local, industrial and foreign air pollution monitoring agencies participate in the surveys.

Sample materials furnished for the audits are designed to simulate the several types of collected air pollution samples as closely as possible. The materials for the manual methods primarily evaluate only the analytical portion of the total air measurement process; i.e., they do not determine errors in sample collection, transportation, handling, storage, and data processing.

Audits are presently conducted twice a year for carbon monoxide, sulfur dioxide, nitrogen dioxide, lead, sulfate and nitrate and once a year for high-volume flow rate. Audits on SO_2 continuous monitors are conducted throughout the year. At the end of the year, a comprehensive report is prepared summarizing the audit results of that year. Each participant is sent a copy of the audit results.

In addition, each laboratory participating in an audit receives an evaluation of its performance shortly after the audit is completed. Laboratories submitting abnormally high or low results are offered an opportunity to analyze another set of samples. However, the retest results are not included in the summary report.

This report presents the results of EPA's ambient air audits for 1981. Approximately 300 laboratories participated in the program. The category and number of participants in each audit are presented in Table 1. This table shows that the number of agencies participating in the 1981 SO_2 and NO_2 bubbler method audits decreased 20 percent from the number participating in the 1980 audits. On the other hand, the number of CO monitors audited increased 20 percent as did the number of participants in the SO_4 and NO_3 audits. Participation in the Pb audit increased 10 percent, but

the flow rate audit participation was up only 2 percent. A total of 159 SO₂ continuous monitors were audited with the SO₂ monitor audit device introduced this year.

Throughout this report, reference is made to "assigned values." These values are the standards against which reported results are gauged and have been so designated after consideration of the analytical results of the referee laboratory, the QAD/EMSL Standards Laboratory, and the manufacturer of the audit material.

SECTION 2

SUMMARY AND CONCLUSIONS

The 1981 results were consistent with those of recent years when mid-range sample results were compared. After removal of outliers, the percentage of results within 20 percent of the assigned values ranged from 82.1 percent for the SO_2 bubbler to 98.5 percent for CO. The overall average was 90.5 percent, which compares closely to the 90.1 percent observed during the 1979, 1980, and 1981 audits.¹

The following percentage of results were rejected as outliers for each type of audit: SO_2 bubbler (10%), NO_2 bubbler (3.8%), CO (3.8%), SO_4 (4.2%), NO_3 (5.0%), Pb (3.0%), and flow rate (3.4%). A similar amount of data was rejected in previous audits. Overall, the results for the last four years show that the level of performance has reached a plateau: i.e., approximately the same number of results are deleted as outliers and the overall precision and accuracy estimates change little from year to year.

SECTION 3

AUDIT MATERIALS

The audit samples span the wide range of pollutant concentrations experienced in ambient air monitoring. This is achieved directly with the CO samples, which are prepared in cylinders. Dilution is necessary for the lyophilized SO₂ and aqueous NO₂ samples in order to obtain the desired concentrations. Lead, NO₃ and SO₄ filter strip samples require both dissolution and dilution to arrive at the needed range of concentrations. The SO₂ continuous monitor audit samples require dilution of the SO₂ with zero air.

Although many air monitoring sites rarely encounter pollutant concentrations at the higher audit sample levels, they are included to assure that monitoring methods are verified at the higher levels.

Each sample type used in the 1981 audits is described in the following paragraphs.

SULFUR DIOXIDE (MANUAL)

Lyophilized samples, composed of sodium sulfite and potassium tetrachloromercurate, simulate ambient air samples collected according to the Pararosaniline Method, the reference method for determining SO₂ in the atmosphere. In these audits, the concentrations ranged from 40 to 200 µg of sulfur dioxide equivalent per cubic meter when reconstituted properly. A sample set consisted of five different concentrations.

NITROGEN DIOXIDE (MANUAL)

Nitrogen dioxide samples consist of aqueous sodium nitrite solutions that simulate ambient NO₂ samples collected by a 24-hour NO₂ bubbler method. Audit results are expressed in terms of micrograms per milliliter (nitrite concentration). These solutions, when properly diluted according to directions, are equivalent to collected atmospheric NO₂ concentrations of approximately 6 to 40 µg/m³. A sample set consists of five different concentrations.

CARBON MONOXIDE

These audit materials consist of a mixture of CO, CO₂ and CH₄ and zero air in a pressurized gas cylinder that simulates an ambient air sample. The concentrations of the three CO samples used in the 1981 audits ranged from 7 to 45 ppm. Directions specify that the gas sample be introduced into a continuous analyzer in the "sample" mode, which permits the analyzer to draw the sample in the same fashion and at the same flow rate as during ambient air monitoring.

SULFATE, NITRATE AND LEAD ON FILTER STRIPS

The filter strip samples used in sulfate, nitrate and lead audits are each 1.9 cm wide by 20 cm long. They are cut from 20-by 25.4-centimeter glass fiber filters that have been spiked with an aqueous solution of the appropriate solution and then oven dried. After analysis, pollutant concentrations are computed by assuming that the samples were collected on the prescribed high-volume filter with a sample air volume of 2,000 m³. Six sample strips comprise a set.

Sulfate and nitrate audit samples are prepared from sodium sulfate and potassium nitrate. Calculated nitrate concentrations ranged from 1 to 12 µg/m³ and sulfate from 1 to 27 µg/m³. Lead samples, which are prepared from lead nitrate ranged in concentration from 0.4 to 9 µg/m³ of lead.

HIGH-VOLUME FLOW RATE (ReF DEVICE)

The reference flow (ReF) device used for audits of high-volume flow rate consisted of a modified orifice, a wind deflector, a manometer, and a series of resistance plates that simulate particulate loading. A single ReF device is supplied to each participating agency with instructions to check samplers at as many sampling sites as feasible within the allotted time.

Each ReF device is calibrated with a positive displacement meter before use. During use, the device is mounted on top of the sampler, replacing the filter face plate. A wind deflector is used to prevent fluctuations in the measurements due to wind blowing across the orifice.

SULFUR DIOXIDE CONTINUOUS MONITORS

Introduced in 1981, the continuous monitor auditing system is an auditing device for SO₂ continuous ambient air monitors. The device is a porous plug dilution system that provides a mechanism whereby controlled quantities of SO₂ and diluent air are continuously combined in a mixing chamber and passed into the monitor. The flow rate of each gas is controlled by maintaining a predetermined pressure drop across the porous plug flow restrictor. Variable SO₂ concentrations are obtained by switching between four restrictors.

The audit device, which is housed in a compact, lightweight, impact-resistant case, is constructed so that only those controls required for system operation are exposed. By opening and closing different toggle valves, it is possible to generate up to five preset pollutant concentrations. Two compressed gas cylinders are supplied with each unit, one as the pollutant source and the other for dilution.

Each audit device is calibrated for flow at all the settings used in the audit. Flow calibrations are referenced to laminar flow elements

traceable to National Bureau of Standards flow standards. Sulfur dioxide concentrations ranging from 0.04 to 0.7 ppm were used in the 1981 audits.

SECTION 4

AUDIT RESULTS

The results of the 1981 audit are presented in Tables 2 through 22. The term "audit mean" in these tables denotes the average of all values reported by the participants for that sample after correcting for outliers. Rejection of results as outliers was based on Chauvenet's Criterion². The percent accuracy (% Acc.) and the precision, as measured by the percent coefficient of variation (% CV), were computed as follows:

$$\% \text{ Acc.} = \frac{\text{audit mean} - \text{EPA assigned value}}{\text{EPA assigned value}} \times 100\%$$

$$\% \text{ CV} = \frac{\text{audit standard deviation}}{\text{audit mean}} \times 100\%$$

SULFUR DIOXIDE

Approximately 60 laboratories participated in the April (0481) and October (1081) audits. The results, with outliers deleted, were used to calculate the mean, percent accuracy, and percent CV values reported in Tables 2 and 3. The corrected data were also used to compute the data in Table 4, which shows the percentage of laboratories that obtained results within ± 10 , 20, 30, and 50 percent of the assigned values.

A significant negative bias is apparent in the two audits, with the means ranging from 1 to 8 $\mu\text{g}/\text{m}^3$ lower than the assigned values presented in Table 2. A similar bias occurred in the previous year's audits. Generally, somewhat lower average accuracy and precision was apparent at the lowest sample concentration.

As shown in Table 3, accuracy ranged from -1.3 to -11.0 percent for the manual pararosaniline method and from 0.0 to -15.2 percent for the automated method. Precision by both the manual and automated methods improved with increased sample concentration, although accuracy was not so dependent on that factor. Two other analytical methods, the West-Gaeke method and the buffered formaldehyde method were used by a few participants, but not in sufficient number to make statistical judgments from the data.

As shown in Table 4, 70 percent or more of the laboratories reported results within ± 20 percent of the assigned values. This correlates well with the 1978, 1979 and 1980 results and indicates that performance in the audit program has leveled off.

NITROGEN DIOXIDE

Approximately 50 laboratories took part in each of the two surveys. With outlier values deleted, the audit mean, percent Accuracy, and percent CV values are given in Tables 5 and 6. The percentage of laboratories that achieved results within ± 10 , 20, 30, and 50 percent of the assigned values is tabulated in Table 7.

Only minor differences between the overall audit averages and the assigned values were observed. Of the 10 samples used in the 2 audits 8 had slightly negative biases and 2 a small positive bias. The differences, which ranged from 0.001 to 0.020 $\mu\text{g NO}_2/\text{mL}$, are in accord with those seen in the 0680 survey, but differ markedly from the December 1980 (1208) audit. In the latter audit a positive bias was observed in all samples.

Overall accuracy, which ranged from -1.7 to 2.3 percent, was quite good in both 1981 audits. The precision of the manual arsenite method improved with increased concentration, but the automated method did not.

A few participants used the Saltzman and TGS-ANSA methods, but the number of results were too small to calculate precision and accuracy estimates.

As shown in Table 7, 95 percent or more of the laboratories' results were from within ± 20 percent of the assigned values. This agrees well with the 0680 audit but is noticeably better than the 1280 audit. This latter audit, however, is unusual because of the positive bias observed in the results.

CARBON MONOXIDE

Approximately 380 monitors were checked in each audit. The actual number of participants was lower, however, because many of them checked more than one instrument. The audit mean, percent Accuracy, and percent CV values are presented in Tables 8 and 9. Table 10 shows the percentage of laboratories that attained results within ± 10 , 20, 30, and 50 percent of the assigned values.

There were considerable differences between the average results for the NDIR and GC methods. For example, accuracy ranged from -1.6 to 0.5 percent in the two audits by the NDIR method and -8.3 to 2.3 percent by the GC method. Because similar results were obtained in both audits conducted the previous year, it is reasonable to conclude that the NDIR method is more accurate in the concentration ranges employed. The methods were essentially the same with respect to precision (percent CV). Other analytical methods used by only a few participants were the gas filter correlation, electrochemical, and selective electrode methods. The number of results reported, however, were not sufficient to calculate precision

and accuracy estimates.

One can see in Table 10 that over 95 percent of the monitors gave results within ± 20 percent of the assigned values, the same as the previous year. The quality of performance has been relatively stable in recent years,¹ indicating that further significant improvement would not be expected.

SULFATE ON FILTER STRIPS

Approximately 50 laboratories participated in each audit. The audit mean, percent accuracy, and percent CV values are tabulated in Tables 11, 12, and 13; and the percentage of laboratories having results within ± 10 , 20, 30, and 50 percent of the assigned values is shown in Table 14. These results have been corrected for outliers.

Accuracy of the manual methods, clearly sensitive to sample concentration, improved at the higher sample concentrations (above $8 \mu\text{g}/\text{m}^3$). At this concentration and above, the barium chloride method was approximately equivalent to the automated methods. All the methods were generally more precise at higher sample concentrations but the Sulfa-Ver[®] method was the one most affected by sample concentration. The barium chloride method was the most imprecise of all.

Other analytical methods used by only a few participants were the manual barium chloranilate and automated barium chloride methods. The number of results, however, were too small to calculate precision and accuracy results.

As shown in Table 14, except for the lowest sample concentration, 75 percent or more of the laboratories reported results within ± 20 percent of the assigned values. This is substantially the same proficiency level achieved in the 1979 and 1980 audits,¹ indicating that performance has leveled off.

NITRATE ON FILTER STRIPS

Approximately 50 laboratories participated in each of the audits. The audit mean, percent accuracy, and percent CV values appear in Tables 15 and 16; the percentage of laboratories having results within ± 10 , 20, 30, and 50 percent of the assigned values is presented in Table 17. The results have been corrected for outliers. Only results by the automated methods are tabulated because of the relatively few manual methods results reported.

There was little difference in accuracy between the ion chromatography and the cadmium reduction methods; both yielded good results.

Precision was distinctly better for the cadmium reduction method in 11 of 12 samples.

Other methods used by a few participants were the manual cadmium reduction, brucine, Szechrome[®] NAS, ultraviolet spectrophotometry, hydrazine, and 2,4 xyleneol methods. The number of results reported, however, was too small to calculate precision and accuracy estimates.

As shown in Table 17, excluding the lowest sample concentration, 80 percent or more of the results were within ± 20 percent of the assigned values. Results from the 1979 and 1980 audits showed essentially an identical analytical proficiency indicating that a constant level of performance has been achieved.

LEAD ON FILTER STRIPS

Approximately 95 laboratories participated in each lead audit. The audit mean, percent accuracy, and percent CV values are shown in Table 18. The percentage of laboratories producing results within ± 10 , 20, 30, and 50 percent of the assigned values is indicated in Table 19. These results have been corrected for outliers.

Good accuracy prevailed in both the 0181 and 0781 audits, although the latter showed a slightly negative bias. Precision varied only slightly in 10 of 12 samples, suggesting that, with respect to precision, the analytical method is largely unaffected by concentration over the range used in the audit. Only one of the laboratories used the X-ray fluorescence method; all others used the atomic absorption method.

As shown in Table 19, aside from one low concentration sample, 90 percent or more of the results were within ± 20 percent of the assigned values. Comparison with the results from the 1979 and 1981 audits shows a similar level of accuracy.¹

SULFUR DIOXIDE (CONTINUOUS MONITORS)

Monitors are replacing the bubbler method for SO_2 because: (1) they offer real-time, continuous values; (2) they are easier to operate; and (3) they are more accurate at the low levels of SO_2 now in the ambient air. Approximately 600 state and local agencies now use SO_2 monitors. For this reason, a device was developed that could audit continuous SO_2 analyzers at concentrations within the normal ambient SO_2 concentration range (0-1 ppm). It was introduced in the National Audit Program in 1981.

Eighty-four laboratories used the new device in 1981 to check 159 monitors (Table 20). The three most commonly audited types of analyzers were fluorescence (104), flame photometric (28), and coulometric (22). The accuracy achieved by each type of monitor is presented in Table 21.

HIGH-VOLUME FLOW RATE

One hundred eighty-eight agencies participated in this program with an average participation of 7.8 sites per agency. The pressure transducer-continuous recorder was the most frequently used measurement method (39.8%), followed by the rotameter (33.8%), pressure transducer/flow controller (5.6%), and the flow controller (4.5%) methods. The remaining methods were mainly orifice manometer, manometer, flow gauge and pressure transducer/noncontinuous methods. The results are summarized in Table 22. A result within ± 4.5 percent of the EPA assigned value was considered to be within the "sample range,"¹ the highest level of proficiency. For example, Table 22 shows that, overall, 30 percent of the flow meters achieved an accuracy within ± 2.5 percent of the assigned value and 50 percent achieved an accuracy within 4.5 percent.

REFERENCES

1. Rhodes, R.C., B. I. Bennett and J. C. Puzak. EPA's National Performance Audit Program for Ambient Air Pollution Measurements. In: Proceedings of the 75th Annual Meeting of the Air Pollution Control Association, New Orleans, Louisiana, 1982. 82-23,7:1-18.
2. Chauvenet, W. A Manual of Spherical and Practical Astronomy. J. B. Lipincott and Company, Philadelphia, Pennsylvania, 1863. pp. 558-566.

TABLE 1. AGENCY PARTICIPATION

Survey	Distribution (%)				No. of Laboratories	No. of Monitors
	States	Local	Industry	Federal		
SO ₂ -- April 1981	34.2	43.8	17.8	2.7	63	NA
SO ₂ -- October 1981	31.1	42.6	21.3	1.6	61	NA
NO ₂ -- June 1981	33.9	46.4	17.9	0.0	56	NA
NO ₂ -- December 1981	34.7	49.0	16.3	0.0	49	NA
CO -- March 1981	45.2	44.1	5.0	1.8	NA	383
CO -- September 1981	45.1	41.9	11.1	1.3	NA	379
SO ₄ -- February 1981	38.1	31.7	20.6	4.8	63	NA
SO ₄ -- August 1981	45.0	26.7	21.7	3.3	60	NA
NO ₃ -- February 1981	38.8	28.6	22.4	4.1	49	NA
NO ₃ -- August 1981	46.8	23.4	23.4	2.1	47	NA
Pb -- January 1981	42.6	26.7	23.8	3.0	102	NA
Pb -- July 1981	42.4	29.3	25	1.1	92	NA
SO ₂ (continuous)	54.1	24.5	12.6	8.8	NA	159
High-Volume Flow-Rate -- May 1981	31.0	48.5	17.5	0.5	NA	1462

NA = Not applicable.

TABLE 2. AUDIT RESULTS FOR SULFUR DIOXIDE

Audit	Level	n*	Assigned value ($\mu\text{g}/\text{m}^3$)	Mean ($\mu\text{g}/\text{m}^3$)	% Acc.	% CV
0481	1	56	46.6	42.9	-7.9	22.8
	2	57	76.6	72.1	-5.9	20.1
	3	51	92.6	88.2	-4.8	13.2
	4	58	147.6	138.4	-6.2	14.0
	5	62	185.3	183.8	-0.8	12.2
1081	1	56	55.4	53.5	-3.4	39.8
	2	59	75.1	70.4	-6.3	36.5
	3	58	98.9	95.2	-3.7	34.9
	4	59	164.4	162.0	-1.5	25.7
	5	59	176.8	170.3	-3.7	26.4

*Survey 0481: Data returned by 63 participants (n).

*Survey 1081: Data returned by 61 participants (n).

TABLE 3. RESULTS FOR THE PARAROSANILINE METHOD

Audit	Level	Assigned value ($\mu\text{g}/\text{m}^3$)	Manual method				Automated method			
			n	Mean ($\mu\text{g}/\text{m}^3$)	% Acc.	% CV	n	Mean ($\mu\text{g}/\text{m}^3$)	% Acc.	% CV
0481	1	46.6	44	44.2	-5.2	29.2	8	39.5	-15.2	23.4
	2	76.6	43	71.9	-6.1	18.6	9	71.3	-6.9	14.0
	3	92.6	40	88.5	-4.4	11.5	7	84.2	-9.1	15.7
	4	147.6	43	138.2	-6.4	12.1	10	142.2	-3.7	9.7
	5	185.3	45	182.6	-1.5	10.2	10	182.4	-1.6	10.4
1081	1	55.4	43	49.3	-11.0	26.2	9	56.4	1.8	11.1
	2	75.1	45	67.8	-9.7	20.3	9	75.1	0.0	10.8
	3	98.9	44	91.9	-7.1	13.4	9	99.1	0.2	7.5
	4	164.4	45	162.2	-1.3	10.6	9	163.3	-0.7	4.4
	5	176.8	44	169.9	-3.9	11.0	9	171.8	-2.8	4.7

TABLE 4. PERCENT OF SULFUR DIOXIDE MEASUREMENTS
WITHIN INDICATED PERCENT OF ASSIGNED VALUES

Audit	Level	Assigned value ($\mu\text{g}/\text{m}^3$)	10%	20%	30%	50 %
0481	1	46.6	44.8	75.9	82.8	91.4
	2	76.6	63.8	79.3	87.9	94.8
	3	92.6	64.2	84.9	90.6	98.1
	4	147.6	66.1	84.7	88.1	100.0
	5	185.3	65.1	85.7	93.7	100.0
1081	1	55.4	37.5	69.6	80.4	87.5
	2	75.1	52.5	72.9	79.7	88.1
	3	98.9	55.2	79.3	89.7	91.4
	4	164.4	67.8	84.7	93.2	93.2
	5	176.8	66.1	89.8	91.5	93.2

TABLE 5. AUDIT RESULTS FOR NITROGEN DIOXIDE

Audit	Level	n*	Assigned value ($\mu\text{g}/\text{ml}$)	Mean ($\mu\text{g}/\text{ml}$)	% Acc.	% CV
0681	1	54	0.200	0.194	-1.5	8.2
	2	55	0.350	0.358	2.3	36.3
	3	54	0.550	0.546	-0.7	10.7
	4	55	0.900	0.886	-1.6	7.6
	5	55	1.240	1.223	-1.4	7.3
1281	1	47	0.291	0.293	0.7	5.8
	2	47	0.494	0.490	-0.8	5.5
	3	47	0.793	0.785	-1.0	3.4
	4	47	0.998	0.982	-1.6	4.9
	5	48	1.202	1.182	-1.7	4.0

*Audit 0681: Data returned by 56 laboratories.
Audit 1281: Data returned by 49 laboratories.

TABLE 6. AUDIT RESULTS FOR NITROGEN DIOXIDE BY THE SODIUM ARSENITE METHOD

Audit	Level	Assigned value ($\mu\text{g/mL}$)	Manual method			Automated method		
			n	Mean ($\mu\text{g/mL}$)	% Acc.	% CV	n	Mean ($\mu\text{g/mL}$) % Acc. % CV
0681	1	0.200	37	0.189	-5.5	19.0	13	0.196 -2.0 5.1
	2	0.350	37	0.365	4.3	42.5	13	0.345 -1.4 5.2
	3	0.550	36	0.547	0.6	12.6	13	0.547 -0.6 5.5
	4	0.900	37	0.891	-1.0	8.3	13	0.882 -2.0 6.0
	5	1.240	36	1.234	-0.5	7.6	13	1.217 -1.8 5.7
1281	1	0.291	30	0.288	-1.0	8.0	12	0.298 2.4 7.4
	2	0.494	29	0.493	-0.2	5.0	13	0.506 2.4 13.8
	3	0.793	30	0.784	-1.1	5.4	13	0.777 -2.0 6.3
	4	0.998	30	0.981	-1.7	4.7	13	0.974 -2.4 6.6
	5	1.202	30	1.189	-1.1	3.1	13	1.156 -3.8 7.3

TABLE 7. PERCENTAGE OF NITROGEN DIOXIDE MEASUREMENTS WITHIN
INDICATED PERCENTAGE OF ASSIGNED VALUE

Audit	Level	Assigned value ($\mu\text{g/mL}$)	10%	20%	30%	50%
0681	1	0.20	72.7	94.5	98.2	98.2
	2	0.35	89.3	94.6	94.6	96.4
	3	0.55	90.9	94.5	96.4	96.4
	4	0.90	85.7	96.4	96.4	98.2
	5	1.24	85.5	96.4	96.4	98.2
1281	1	0.291	91.7	97.9	97.9	100.0
	2	0.494	89.6	97.9	97.9	100.0
	3	0.793	93.9	98.0	100.0	100.0
	4	0.998	93.9	100.0	100.0	100.0
	5	1.202	93.9	100.0	100.0	100.0

TABLE 8. AUDIT RESULTS FOR CARBON MONOXIDE

Audit	Level	n	Assigned value (ppm)	Mean (ppm)	% Acc.	% CV
0381	1	373	6.98	6.86	-1.7	7.0
	2	381	25.1	25.1	0.0	3.2
	3	379	43.9	44.0	0.2	3.1
0981	1	360	13.6	13.6	0.0	5.8
	2	373	28.2	28.3	1.1	4.8
	3	371	41.1	41.1	0.0	4.6

Audit 0381: Data returned for 383 monitors.

Audit 0981: Data returned for 379 monitors.

TABLE 9. AUDIT RESULTS FOR CARBON MONOXIDE BY THE NDIR AND GC METHODS

Audit	Level	Assigned value (ppm)	NDIR			GC				
			n	Mean (ppm)	% Acc.	% CV	n	Mean (ppm)	% Acc.	% CV
0381	1	6.98	355	6.87	-1.6	7.4	10	6.40	-8.3	8.4
	2	25.1	359	25.2	0.4	3.2	10	25.4	1.2	5.3
	3	43.9	357	44.1	0.5	2.8	10	44.9	2.3	4.7
0981	1	13.6	346	13.6	0.0	4.9	5	13.0	-4.4	4.5
	2	28.2	358	28.3	0.4	3.7	5	27.7	-1.8	2.7
	3	41.1	356	41.2	0.2	3.6	5	40.7	-1.0	2.4

TABLE 10. PERCENTAGE OF CARBON MONOXIDE MEASUREMENTS WITHIN
INDICATED PERCENTAGE OF ASSIGNED VALUE

Audit	Level	Assigned value (ppm)	10%	20%	30%	50%
0381	1	6.98	83.4	96.8	98.9	99.2
	2	25.1	97.4	99.5	99.5	99.5
	3	43.9	96.9	99.5	99.5	99.5
0981	1	13.6	93.2	96.7	97.3	98.1
	2	28.2	95.5	97.4	97.9	98.4
	3	41.1	95.0	97.6	97.9	98.4

TABLE 11. AUDIT RESULTS FOR SULFATE ON FILTERS STRIPS

Audit	Level	n*	Assigned value ($\mu\text{g}/\text{m}^3$)	Mean ($\mu\text{g}/\text{m}^3$)	% Acc.	% CV
0281	1	60	22.8	22.5	-1.3	14.5
	2	60	10.2	10.5	2.9	16.6
	3	61	6.0	6.5	8.3	19.1
	4	60	1.8	2.5	38.9	39.6
	5	60	18.6	18.2	-2.2	12.6
	6	60	14.4	14.3	-0.7	15.5
0881	1	54	1.2	1.6	33.3	55.0
	2	57	4.8	5.1	6.3	34.3
	3	58	7.8	8.1	3.8	25.6
	4	58	12.6	12.7	0.8	12.6
	5	59	21.0	21.0	0.0	9.5
	6	59	27.0	27.5	1.9	16.6

*Audit 0281: Data returned by 63 laboratories.
 Audit 0881: Data returned by 60 laboratories.

TABLE 12. AUDIT RESULTS FOR SULFATE BY THE MANUAL METHODS

Audit	Level	Assigned value ($\mu\text{g}/\text{m}^3$)	BaCl_2			Sulfa-Ver		
			n	Mean ($\mu\text{g}/\text{m}^3$)	% Acc.	% CV	n	Mean ($\mu\text{g}/\text{m}^3$) % Acc. % CV
0281	1	22.8	15	23.3	2.2	35.6	5	24.0 5.3 11.8
	2	10.2	15	11.3	10.8	24.5	5	11.5 12.7 16.8
	3	6.0	15	6.3	5.0	22.4	5	7.7 28.3 20.3
	4	1.8	15	2.5	38.9	34.8	5	3.8 111.1 58.5
	5	18.6	15	19.4	4.3	26.0	5	20.9 12.4 8.2
	6	14.4	15	15.1	4.9	25.2	5	16.2 12.5 12.0
0881	1	1.2	12	1.9	58.3	63.7	7	1.8 50.0 54.2
	2	4.8	13	5.2	8.3	24.9	7	4.6 -4.2 17.3
	3	7.8	13	8.2	5.1	18.7	7	7.8 0.0 16.5
	4	12.6	14	13.1	4.0	12.2	7	11.8 -6.3 8.3
	5	21.0	14	21.3	1.4	9.3	7	19.7 -6.2 6.1
	6	27.0	14	26.9	-0.4	9.0	7	27.0 0.0 13.7

TABLE 13. AUDIT RESULTS FOR SULFATE BY THE AUTOMATED METHODS

Audit	Level	Assigned value ($\mu\text{g}/\text{m}^3$)	Methyl Thymol Blue				Ion Chromatograph			
			n	Mean ($\mu\text{g}/\text{m}^3$)	% Acc.	% CV	n	Mean ($\mu\text{g}/\text{m}^3$)	% Acc.	% CV
0281	1	22.8	23	22.2	-2.6	4.5	15	22.6	-0.9	4.6
	2	10.2	23	10.2	0.0	4.6	15	10.3	1.0	13.0
	3	6.0	23	6.2	3.3	11.1	15	6.2	3.3	12.0
	4	1.8	23	2.2	22.2	17.6	15	2.3	27.8	32.2
	5	18.6	23	17.9	-3.8	7.2	15	17.6	-5.4	10.6
	6	14.4	23	14.0	-2.8	5.1	15	14.6	1.4	7.9
0881	1	1.2	23	1.2	0.0	36.7	13	1.7	41.7	58.8
	2	4.8	23	4.7	-2.1	12.2	12	4.8	0.0	9.3
	3	7.8	23	7.5	-3.8	8.4	13	7.7	-1.3	4.4
	4	12.6	23	12.3	-2.4	6.2	12	12.4	-1.6	5.8
	5	21.0	23	20.9	-0.5	7.4	13	20.8	-1.0	6.2
	6	27.0	23	27.7	2.6	20.1	13	27.1	0.4	6.8

TABLE 14. PERCENTAGE OF SULFATE MEASUREMENTS WITHIN
INDICATED PERCENTAGE OF ASSIGNED VALUES

Audit	Level	Assigned value ($\mu\text{g}/\text{m}^3$)	10%	20%	30%	50%
0281	1	22.8	73.0	84.1	85.7	93.7
	2	10.2	69.8	81.0	85.7	92.1
	3	6.0	60.3	77.8	82.5	92.1
	4	1.8	24.2	45.2	46.8	74.2
	5	18.6	68.3	85.7	90.5	95.2
	6	14.4	73.0	84.1	88.9	93.7
0881	1	1.2	32.1	42.9	53.6	64.3
	2	4.8	56.9	79.3	82.8	93.1
	3	7.8	64.4	84.7	91.5	96.6
	4	12.6	67.8	91.5	94.9	96.6
	5	21.0	80.0	95.0	96.7	98.3
	6	27.0	78.3	91.7	95.0	95.0

TABLE 15. AUDIT RESULTS FOR NITRATE ON FILTERS STRIPS

Audit	Level	n*	Assigned value ($\mu\text{g}/\text{m}^3$)	Mean ($\mu\text{g}/\text{m}^3$)	% Acc.	% CV
0281	1	46	11.4	10.9	-4.4	13.0
	2	46	5.1	5.2	2.0	15.0
	3	45	3.9	3.8	-2.6	16.3
	4	46	0.9	1.0	11.1	38.0
	5	47	9.0	8.8	-2.2	16.5
	6	45	7.2	7.1	-1.4	13.1
0881	1	45	0.6	0.8	33.3	72.5
	2	44	2.4	2.5	4.2	20.0
	3	46	4.2	4.5	7.1	38.0
	4	45	6.0	6.1	1.7	13.1
	5	46	8.7	8.7	0.0	8.7
	6	46	12.6	12.5	-0.8	11.0

*Audit 0281: Data returned by 49 laboratories.

Audit 0881: Data returned by 47 laboratories.

TABLE 16. AUDIT RESULTS FOR NITRATE BY THE AUTOMATED METHODS

Audit	Level	Assigned value ($\mu\text{g}/\text{m}^3$)	n	Ion Chromatography			n	Cadmium Reduction		
				Mean, ($\mu\text{g}/\text{m}^3$)	% Acc.	% CV		Mean, ($\mu\text{g}/\text{m}^3$)	% Acc.	% CV
0281	1	11.4	15	11.1	-2.6	14.6	18	11.2	-1.8	3.8
	2	5.1	15	5.1	0.0	17.5	18	5.1	0.0	3.7
	3	3.9	15	3.9	0.0	17.3	18	3.8	-2.6	15.2
	4	0.9	15	1.1	22.2	53.1	18	1.2	33.3	64.7
	5	9.0	15	8.6	-4.4	19.2	18	9.0	0.0	4.8
	6	7.2	15	7.4	2.8	10.5	18	7.1	-1.4	3.8
0881	1	0.6	12	0.7	16.7	57.7	15	0.7	16.7	37.5
	2	2.4	12	2.6	8.3	30.5	15	2.4	0.0	3.8
	3	4.2	12	4.1	-2.4	10.8	16	4.2	0.0	4.8
	4	6.0	11	6.0	0.0	9.7	16	6.1	1.7	9.1
	5	8.7	12	8.5	-2.3	7.7	16	8.7	0.0	5.4
	6	12.6	12	12.7	0.8	9.1	16	12.6	0.0	5.6

TABLE 17. PERCENTAGE OF NITRATE MEASUREMENTS WITHIN INDICATED
PERCENTAGE OF ASSIGNED VALUE

Audit	Level	Assigned value ($\mu\text{g}/\text{m}^3$)	10%	20%	30%	50%
0281	1	11.4	79.6	83.7	87.8	93.9
	2	5.1	77.6	81.6	83.7	91.8
	3	3.9	69.4	79.6	81.6	89.8
	4	0.9	38.3	57.4	72.3	80.9
	5	9.0	73.5	81.6	85.7	93.9
	6	7.2	71.4	83.7	87.8	89.8
0881	1	0.6	39.1	54.3	67.4	82.6
	2	2.4	75.6	84.4	91.1	93.3
	3	4.2	74.5	91.5	93.6	95.7
	4	6.0	73.9	87.0	95.7	95.7
	5	8.7	83.0	93.6	95.7	97.9
	6	12.6	74.5	91.5	95.7	97.9

TABLE 18. AUDIT RESULTS FOR LEAD ON FILTER STRIPS

Audit	Level	n*	Assigned value ($\mu\text{g}/\text{m}^3$)	Mean ($\mu\text{g}/\text{m}^3$)	% Acc.	% CV
0181	1	95	0.59	0.60	1.7	8.3
	2	100	2.04	2.07	1.5	7.7
	3	100	3.48	3.55	2.1	7.3
	4	99	4.98	4.98	0.0	6.8
	5	101	6.58	6.57	-0.2	8.4
	6	96	7.95	7.86	-1.1	5.7
0781	1	90	0.45	0.43	-4.4	20.9
	2	88	2.10	2.07	-1.4	8.2
	3	91	3.90	3.77	-3.3	15.6
	4	88	5.55	5.48	-1.3	7.7
	5	89	7.35	7.19	-2.2	7.5
	6	90	9.00	8.82	-2.0	8.2

*Audit 0181: Data returned by 102 laboratories.

Audit 0781: Data returned by 92 laboratories.

TABLE 19. PERCENTAGE OF LEAD MEASUREMENTS WITHIN INDICATED
PERCENTAGE OF ASSIGNED VALUE

Audit	Level	Assigned value ($\mu\text{g}/\text{m}^3$)	10%	20%	30%	50%
0181	1	0.59	73.7	92.9	96.9	99.0
	2	2.04	81.2	96.0	98.0	99.0
	3	3.48	88.1	96.0	98.0	99.0
	4	4.98	90.1	96.0	97.0	98.0
	5	6.58	84.3	94.1	98.0	99.0
	6	7.95	97.9	97.0	97.0	99.0
0781	1	0.45	56.5	82.6	88.0	93.5
	2	2.10	82.4	94.5	95.6	96.7
	3	3.90	84.8	95.7	96.7	96.7
	4	5.55	88.9	95.6	96.7	97.8
	5	7.35	84.6	94.5	96.7	97.8
	6	9.00	85.9	94.6	95.7	97.8

TABLE 20. AUDIT RESULTS FOR SULFUR DIOXIDE CONTINUOUS MONITORS

Flow setting	Number of reported values	Range of assigned values (ppm)	Mean differences	
			ppm	% diff
1	32	0.617 to 0.721	-0.050	-7.1
2	148	0.401 to 0.519	-0.023	-4.9
3	159	0.204 to 0.291	-0.012	-4.7
4	159	0.165 to 0.221	-0.009	-4.8
5	157	0.039 to 0.070	-0.003	-4.7
6	159	0.000	+0.001	----

TABLE 21. AUDIT RESULTS FOR SULFUR DIOXIDE CONTINUOUS MONITORS
BY VARIOUS INSTRUMENTAL METHODS

Flow setting	Flame photometric average difference			Fluorescent average difference			Coulometric average difference		
	n*	ppm	%	n*	ppm	%	n*	ppm	%
1	7	-0.060	-9.2	17	-0.002	-0.3	4	-0.072	-10.6
2	26	-0.025	-5.4	96	-0.014	-3.0	18	-0.019	-2.1
3	28	-0.021	-8.4	104	-0.006	-2.4	19	-0.014	-5.5
4	28	-0.018	-9.7	94	-0.004	-2.2	19	-0.011	-5.7
5	26	-0.009	-13.5	101	-0.002	-2.4	20	-0.005	-8.3
6	28	0.005	--	104	-0.001	--	22	-0.000	--

*No. of values remaining after outliers deleted.

TABLE 22. AUDIT RESULTS FOR HIGH-VOLUME FLOW RATE

Method	No. of reported results	Results within indicated assigned value (%)			
		30%	50%	70%	90%
Rotameter (visifloat)	2998 ¹	2.21	3.88	6.27	11.47
Pressure transducer(continuous)	2797 ²	2.09	4.06	6.47	12.29
Flow controller	66 ³	2.50	4.52	6.39	10.53
Pressure transducer/flow controller	77 ⁴	2.20	3.09	4.19	6.60
All methods	5882 ⁵	2.08	3.84	6.23	11.33

¹3072 measurements reported²2860 measurements reported³66 measurements reported⁴82 measurements reported⁵6082 measurements reported